Communications

On the Diamagnetic Anisotropy of Metal-free Phthalocyanine

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It is shown, with reference to the diamagnetic anisotropy of metal-free phthalocyanine, that Pauling's model is liable to over-estimate the effective number of π-electrons in aromatic hydrocarbons.

IT has now become evident that the diamagnetic anisotropy (ΔK) of aromatic hydrocarbons is not entirely due to mobile π-electrons the contributions from σ-electrons and other local paramagnetic and diamagnetic terms are also very significant. The semi-classical model of Pauling[1] and the molecular orbital approach of London[2] have both been criticized on the above ground, since these models assume that the entire anisotropy of such systems is due to mobile π-electrons alone. There is, however, another kind of inherent defect in Pauling's model which is not often realized. Salem[3] has discussed it by considering a hypothetical case when, say, six extra electrons are added to benzene. The total ring current in such a case on London's model will be zero; however, on Pauling's semi-classical model it will be twice the magnitude of that in benzene. Actually as additional electrons are added they go to anti-bonding orbitals and give rise to ' paramagnetic ' ring currents which are equal but opposite in sign to the normal ring currents due to bonding electrons. In other words the effect of adding an extra electron to any such system is that it forms electron pair with the π-electrons available at that site, thereby reducing the total anisotropy by an amount which corresponds to that of two π-electrons.

The experimental situation where the above limitation of Pauling's model is realized is not very readily available. However metal-free phthalocyanine (H_2Pc) appears to provide one such situation. H_2Pc is almost perfectly planar[4] and contains four peripheral benzene rings and an inner 16-membered C_8N_8 micro-ring (Fig. 1). We have reported[5] the diamagnetic anisotropy of this crystal and have shown that, on the basis of X-ray structural data and MO calculations, it is a good approximation to treat H_2Pc as four benzene rings isolated from the inner C_8N_8 macro-ring by single bonds, so that it is reasonable to separate the total ΔK into two parts, one due to the macro-ring and the other due to the four benzene rings.

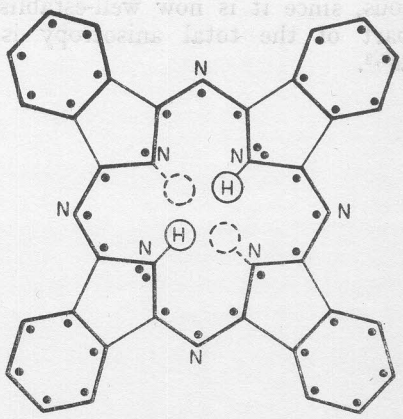


Fig. 1 — Molecular structure of metal-free phthalocyanine [The unlabelled atoms are carbon. Hydrogen atoms associated with benzene rings are not shown]

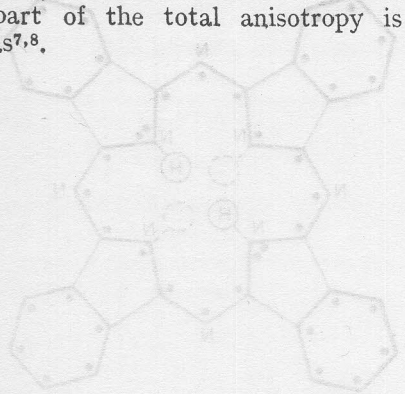
The total diamagnetic anisotropy of H_2Pc is measured[5] to be $(K_\perp - K_{11}) = 610 \times 10^{-6}$ cm^3/mole. Using the experimental value of 60×10^{-6} for the ΔK of benzene[6], the ΔK for the inner C_8N_8 macro-ring becomes: $(\Delta K)_{C_8N_8} = 610 - (60 \times 4) = 370 \times 10^{-6}$. The inner macro-ring has 8 nitrogen and 8 carbon atoms, each contributing one π-electron except the two nitrogen atoms bonded to hydrogen atoms which contribute two π-electrons each. Thus there are 18 π-electrons in this 16-membered macro-ring system. Pauling's model treats all these 18 π-electrons free and contributing in the same sense to ΔK. In the molecular orbital model of London, ΔK is given by

$$\Delta K = 2\beta\left(\frac{2\pi e}{hc}\right)\frac{S^2}{N^2}\cos\frac{2\pi p}{N} \qquad \ldots(1)$$

Here $N=16$. For the C_8N_8 ring with 18 π-electrons $p = 0, \pm 1, \pm 2, \pm 3$ and ± 4 are filled. It would readily appear from Eq. (1) that only 14 π-electrons contribute to ΔK as the 4 π-electrons in the $p = \pm 4$ orbital do not contribute to ΔK, the cos $2\pi p/N$ term becoming zero for $p = \pm 4$. It can be seen easily that two π-electrons of the C_8N_8 macro-ring occupy anti-bonding orbital, thus reducing, the effective number of π-electrons to 14. Obviously the discrepancy in predicting the correct number of the effective π-electrons between the molecular orbital and Pauling's method arises because the latter treats all the π-electrons to be contributing to ΔK and fails to realise that the two π-electrons associated with each of the two nitrogen atoms, bonded to the hydrogen atoms, get paired and do not contribute to ΔK.

A calculation of ΔK for the C_8N_8 macro-ring on Pauling's theory using 18 π-electrons gives a value 470×10^{-6} as against the exprimental value of

370×10^{-6}. Assuming only 14 π-electrons as effective Pauling's theory, however, yields $\Delta K=367\times10^{-6}$. As expected Eq. (1) gives a very low absolute value for ΔK, but reasonable agreement is obtained when compared as $(\Delta K_{C_9N_8}/\Delta K_{Benzene})$ ratio. A SCF-MO calculation[5] also yields $\Delta K=220\times10^{-6}$ which is only about 60% of the experimental value. The close agreement obtained above on Pauling's theory using 14 π-electrons must be considered as fortuitous, since it is now well-established that only a part of the total anisotropy is due to π-electrons[7,8].



References

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